- Technical Paper -

THE EFFECT OF FLY ASHES ON THE ASR MITIGATION IN CONCRETE WITH COMBINATION OF CALCIUM CARBONATE AGGREGATE AND ANDESITE AGGREGATE

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ABSTRACT

This study focuses on the ASR mitigation effect of fly ashes in concrete with a different proportion of non-reactive and reactive aggregate. Accelerated mortar bars and concrete prisms according to JIS and Danish test method were conducted. Proportion of 40% andesite and 60% calcium carbonate shows a pessimum effect. However, the addition of fine fly ashes shows a good ASR mitigation effect which the expansion ratio categorized as "innocuous". In addition, a post analysis such as uranyl fluorescence method and polarizing microscopic observation were adding confidence with these results.

Keywords: ASR, Fine Fly Ashes, Accelerated Curing Test, Polarizing Microscopic Observation

1. INTRODUCTION

It is well known that there are three requirements, at least, for alkali-silica reactions (ASR) occur in concrete which are source of alkali, reactive silica in the aggregate and sufficient moisture. Therefore, in Japan, the use of aggregate and alkali content inside the ready-mixed concrete have to comply with JIS A5308 standard. However, in some cases of ASR, cracking due to ASR also occurred even by limiting the total alkali content of less than 3 kg/m^3 according to JIS A5308. In addition, there are problems in assuring the quality control and diversity of aggregate in Japan [1]. The volcanic rock type such as andesite was a typical reactive aggregate in Japan, which has been damaging a lot of structures due to ASR.

In terms of reactive aggregate, researchers have also found out that certain proportion of reactive aggregate in concrete can influence ASR expansion ratio. This is referred as the "pessimum proportion". In a fixed concentration of alkali, a certain proportion of reactive aggregate will make the expansion become maximum and the expansion will be reduced when the proportion is increased or decreased. It can be explained that the increasing of the reactive aggregate will also followed by the increasing of expansive alkali silicate. However, the addition of more reactive aggregate will decrease the available alkalis to react with, which will decrease the expansive alkali silicate. In addition, although most of those researches are using a fixed concentration of alkali, the pessimum effect was also observed in experimental works with the supply of alkali was unlimited [2].

Beside the pessimum proportion effect, Stanton also found out that different grain size of reactive aggregate caused a different expansion ratio of concrete [3]. In line with that, Ichikawa proposed a new ASR model which demonstrated that the expansion also depends on the size of aggregate particles. However, the increase of particle size of the reactive aggregate will decrease the rate of ASR [4]. Moreover, results from Multon, et al. show that no expansion was measured on the mortars using small particles (under 80 μm) while the coarse particles (0.63–1.25 mm) gave the largest expansions [5]. In general, it believes that sizes of 0.5 to 2 mm of reactive aggregates will cause a significant expansion [4].

Furthermore, some of research works confirmed the mitigation effect of supplementary cementitious materials (SCMs), such as fly ashes and ground granulated blast-furnace slag, for mitigating ASR in concrete [6]. Especially for fly ashes, it is due to three dominant ASR mitigation mechanisms, which are alkali binding, limiting mass transport and improving tensile strength [7]. Other research works have reported that ASR expansion can be more effectively reduced by finer fly ashes with large amounts of amorphous silica glass [8]. Moreover, experiments on mortar bars using andesite stone from Noto Peninsula, Japan, have verified the effectiveness of fly ashes to suppress ASR [9].

In this paper, the main research work is to investigate the effect of high quality fine fly ashes on the ASR mitigation in concrete with combination of reactive aggregate and non-reactive aggregate. As the reactive aggregate, andesite aggregate from Sapporo Japan will be used and the calcium carbonate aggregate will be used as the non-reactive aggregate. The experiments conducted with accelerated concrete prisms test according to JIS and Danish test method. In addition, the reactivity of andesite aggregate and the effect of fly ashes to mitigate ASR with different alkali amount

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inside the pore solution will also be discussed. For this purpose, accelerated mortar bar experiment according to JIS A1146 mortar bar test method was also conducted.

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2. EXPERIMENTS

2.1 Materials

Ordinary portland cement (OPC), from T Co, Ltd., (density: 3.16 g/cm^3, blaine specific surface area: 3.300 cm^2/g) were used. High quality fine fly ashes (FA) from Nanao-ohta coal-burning power plant product, I-type fly ashes classified by JIS A6201, was used as a mineral admixture (density: 2.44g/cm^3, blaine specific surface area: 4.780cm^2/g, Ig.loss: 2.0%). The crushed andesite stone produced in Hokkaido was selected as the reactive aggregate. The alkali-silica reactivity of this stone was assessed by chemical test according to JIS A1145 (Sc: 688mmol/l, Rc: 78mmol/l, Sc/Rc= 8.8) and mortar bar test according to JIS A 1146, both assessed as “deleterious”. This andesite has higher Sc/Rc ratio compared to andesite from Noto Peninsula with Sc/Rc ratio around 2.36 to 4.45 [9]. The reactive components of this andesite stone were cristobalite, tridymite and little glass phases. The calcium carbonate aggregate was used as the non-reactive aggregate, which is composed of more than 95% calcite ($CaCO_3$). The chemical compositions of fly ashes and andesite aggregates are shown in Table 1 and 2, respectively. Fig. 1 shows the polished thin section image of the andesite stone and Fig. 2 shows the particle shape of classified fly ashes.

2.2 Mix Proportions

2.2.1 Mortar bar test

The specimens consist of two mix proportions, OPC and additional 15% of high quality fine fly ashes, according to JIS A1146 test method. Water to binder ratio was set at 50%. In each mix proportion, NaOH was added for making the total alkali content equal to 1.2%, 1.8% and 2.4%. The dimension of mortar bar specimens is 40 × 40 × 160mm. The mixture proportions of mortar bars specimens are listed in Table 3.

2.2.2 Concrete prism test

The specimens consist of two mix proportions which are OPC and additional 15% of high quality fine fly ashes. There are three combination of andesite aggregate (AD) and calcium carbonate aggregate (CC) in each mix proportion. Water to binder ratio was set at 50% for all mix proportion. For concrete prism specimens tested in JIS method, NaOH was added for making the total alkali content equal to 1.2% Na_2Oeq. The dimension of concrete prism specimens is 75 × 75 × 400mm. The mixture proportions of concrete prism specimens are listed in Table 4.

Table 1 Chemical compositions of FA (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	Na_2O	K_2O	Total
FA	53.6	28.9	6.7	3.2	0.8	1.4	0.1	0.2	0.3	0.7	96.2

Table 2 Chemical compositions of Andesite Aggregate (%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	SO_3	Na_2O	K_2O	Total
Andesite Aggregate	61.6	20.3	6.0	5.0	1.0	0.6	0.1	0.2	2.5	2.4	99.7

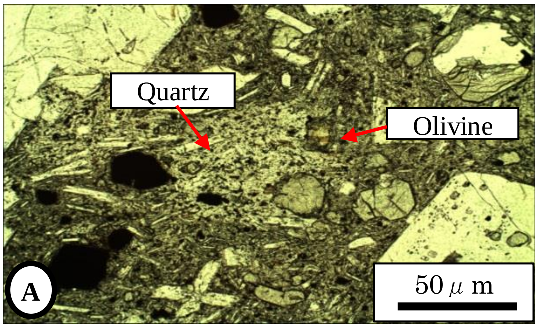
Table 3 Mixture proportions of mortar bar specimens

Specimen Type	W/B	Na2Oeq	Unit amount（kg/m3）				
			Water	NaOH*	Cement	Fly Ashes	Crushed Andesite Stone
1.2OPC	50	1.2 %	227	5	781	-	1758
1.2FA			247	4	664	117	1758
1.8OPC	50	1.8 %	328	2	781	-	1758
1.8FA			332	2	664	117	1758
2.4OPC	50	2.4 %	297	3	781	-	1758
2.4FA			301	3	664	117	1758

*1N NaOH for specimen with 1.2% Na_2Oeq and 5N NaOH for specimen with 1.8% and 2.4% Na_2Oeq

Table 4 Mixture proportions of concrete prism specimens

Specimen Type	Slump（cm）	Air content（%）	W/B（%）	s/a（%）	Unit amount（kg/m^3）						
					Water	Cement	Fly Ashes	Andesite		Calcium Carbonate	
								Fine	Coarse	Fine	Coarse
AD+CC	10±2	2±1	50	40	175	350	0	-	1098	723	-
CC+AD	10±2	2±1	50	40	175	350	0	728	-	-	1111
AD+AD	10±2	2±1	50	40	175	350	0	728	1098	-	-
AD+CC FA	10±2	2±1	50	40	175	298	52	-	1090	718	-
CC+AD FA	10±2	2±1	50	40	175	298	52	723	-	-	1103
AD+AD FA	10±2	2±1	50	40	175	298	52	723	1090	-	-



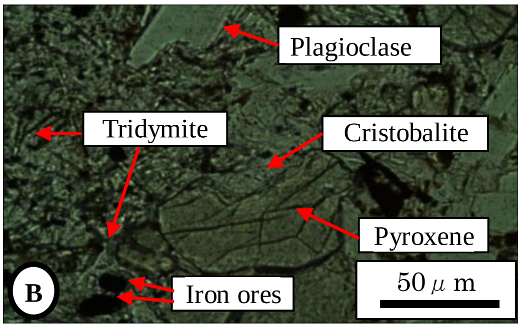


Fig 1. The polished thin section image of andesite stone showing (A) Quarzt and Olivine, (B) Cristobalite, Tridymite, Plagioclase, Pyroxene and Iron ores

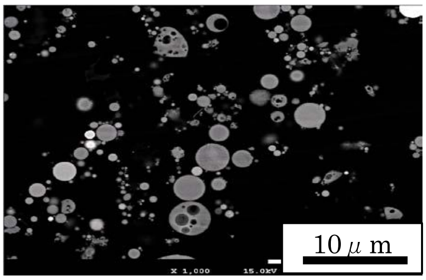


Fig 2. The particle shape of classified fine fly ashes

2.3 Test Methods

2.3.1 Accelerated expansion test

The tests were conducted according to JIS A1146 for mortar bar. For concrete prism, the alkali amount was set in two ways, which are as a fixed amount inside (JIS method) and unlimited supplied from the outside (Danish method). In JIS method, because the cement and fly ashes are containing different forms of alkali and different effect on the ASR [10], thus the addition of 1N sodium hydroxide solution was given to adjust the specimens with equivalent amounts of 1.2% Na_2Oeq. For mortar bar specimens, the equivalent amounts of 1.8% and 2.4% Na_2Oeq were also added. The specimens were cured in fog chamber at 40ºC, and more than 95% of relative humidity. Length change was measured at 20ºC. The expansion ratio over 0.05% for 3 months or over 0.1% for 6 months indicates "deleterious".

In Danish method, without adjusting the amount of alkali, the specimens were immersed in saturated sodium chloride solution at temperature of 50ºC. Length change was measured at 20ºC. The expansion ratio under 0.1% for 3 months indicates "innocuous", between 0.1% to 0.4% "both innocuous and deleterious coexist" and over 0.4% considered as "deleterious".

Moreover, the dynamic modulus elasticity of concrete prism specimens also carried out. This measurement was conducted to study the deterioration process of concrete due to ASR.

2.3.2 ASR gel observation

After accelerated concrete test has been conducted, ASR gel observation by newly developed uranyl acetate fluorescence method, with low concentrations of standard uranyl nitrate solution (commercially available), was carried out. Using UV light radiation, the amount and distribution area of ASR gel, a greenish-yellow coloration area, can be observed.

Table 5 Assessment of petrographic classification of ASR severity of each stage

Stages	The Progress and Severity of ASR
I	The formation of reaction rims and exudation of ASR sol/gel around the reacted aggregate
II	The formation of ASR gel-filled cracks within reacted aggregate
III	The propagation of ASR gel-filled cracks (max < 25μm) from the reacted aggregate into surrounding cement paste
IV	The formation of ASR gel-filled cracks (max 25-50μm) network and the migration of ASR gel into air voids
V	The formation of ASR gel-filled cracks (>50μm) network and the migration of ASR gel into air voids

2.3.3 Polarizing microscopic observation

After the completion of accelerated expansion tests, polished thin section samples with 20μm thickness were prepared. The samples were observed to determine ASR gel and cracking by polarizing light microscopy. Classification of ASR deterioration using thin section was according to Table 5 with the reference by Katayama studies [11].

3. RESULTS AND DISCUSSION

3.1 Expansion Results

3.1.1 Mortar bar test

As can be seen in Fig. 3, the expansion ratio of all specimens tends to be larger in accordance with the addition of alkalis inside the specimens. The expansion ratios of specimens using cement only are exceeding 0.1% after 6 months regardless of its alkali amount. This result may verify the high reactivity of the andesite aggregate which is produced in Hokkaido. Starting from the early stage, the ASR rate was very fast which is completed in just 4 weeks.

In the contrary, specimen with 15% of fly ashes replacement ratio is still enough to mitigate ASR expansion with 1.2% Na_2Oeq. As well as the addition of alkali amount, the expansion is become larger and the ASR mitigation mechanism of 15% of fly ashes replacement ratio almost cannot be seen. However, it could be seen that the ASR rate increases gradually for specimens with additional fly ashes. It proofed the alkali binding capacity of CSH with a low ratio Ca/Si produced from the pozzolanic reaction between fly ashes and portland cement. This CSH can bind available alkalis in the pore solution to minimize the reaction with the reactive aggregate.

3.1.2 Concrete prism test

Figs. 4 and 5 show the expansion ratio of concrete in accelerated expansion test, respectively. In JIS test method, an interesting phenomenon is occurred. The specimen with the andesite aggregate as the fine aggregate (CC+AD) is the only specimen that expands. The expansion exceeds 0.3% after 6 months that might be categorized as "deleterious". The only possible explanation is that the "pessimum effect" occurred on CC+AD specimen. As the particle size of fine aggregate is less than 4.75 mm, this particle size considered to give a significant influence for pessimum size effect. Actually, due to its limited alkali content (1.2% Na_2Oeq) in all specimens, this alkali amount inside the concrete pore system is not sufficient enough to react with the available reactive aggregates. Therefore, the specimens with the reactive aggregate as the coarse aggregate (AD+CC) and as both aggregate (AD +AD) show no expansion. The increase of the aggregate size and the portion of reactive aggregate decrease the available alkalis to form ASR. Another explanation is that increasing the aggregate size and the portion of reactive aggregate will increase the consumption of $Ca(OH)_2$ by mature alkali silicate gel, which can suppress the reaction rims that formed [4].

This phenomenon can more clearly visible for specimens tested according to Danish test method. The result shows the same expansion behavior with the result obtained in JIS test method. The CC+AD specimen was severely damaged by ASR due to the pessimum effect. In addition, in the Danish test method, continuously being supplied with alkalis from the outside make the pore solution filled with unlimited alkalis. Thus trigger much more available alkali to react with the reactive aggregate. Therefore, the expansion ratio of CC+AD specimen was larger compared with the result tested in the JIS test method. The expansion ratio is more than 0.5% after 3 months that can be categorized as "deleterious". The AD+CC and AD +AD specimens also expanded. After 3 months the expansion ratios exceeded 0.1% that can be categorized as "both innocuous and deleterious coexist".

On the other hand, the expansion ratios of specimens with the addition of high quality fine fly ashes were below 0.1% after 3 months, regardless of its reactive aggregate proportion. Once again, high quality fly ash shows a good alkali binding capacity due to the CSH with a low Ca/Si ratio around 0.9. This CSH is better in binding alkalis and thus prevent the ASR to form. It also due to the pozolanic reaction between fly ashes and portland cement reduce the porosity of the concrete thus make the concrete denser. The important point of this high quality fly ashes is its finesse. Finer fly ashes will increase the pozzolanic activity. Moreover, this fly ash also contains more silica and less CaO which is proved to show better ASR mitigation effect.

In addition, for Danish method, the immersion time was extended until 6 months for all specimens. The expansion ratio of all specimens tends to increase sharply except for AD+CC FA and AD +AD FA which are still can be categorized as "innocuous". It seems that, when the surface had deteriorated by ASR and the first crack occurred, the alkali was able to penetrate into the specimens. Thus, the expansion ratio continues to increase. Overall, the additional of high quality fine fly ash is still showing a good ASR mitigation effect.

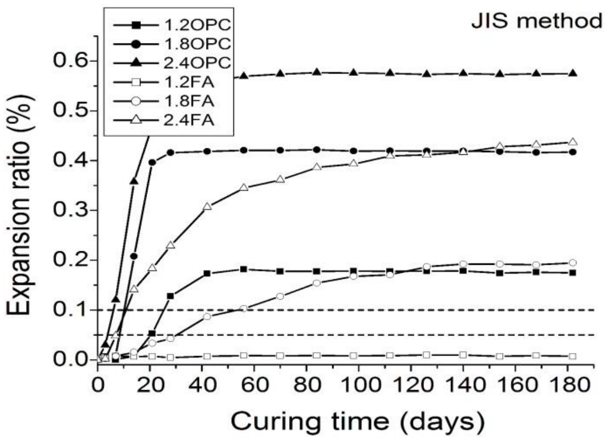


Fig 3. Expansion ratio of mortar bars with different alkali content

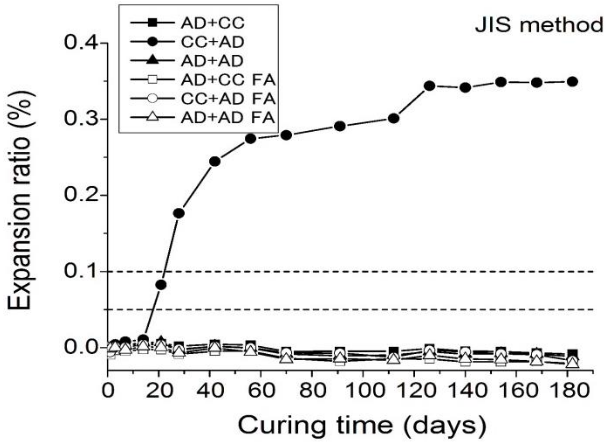


Fig 4. Expansion ratio of concrete prisms tested in JIS test method

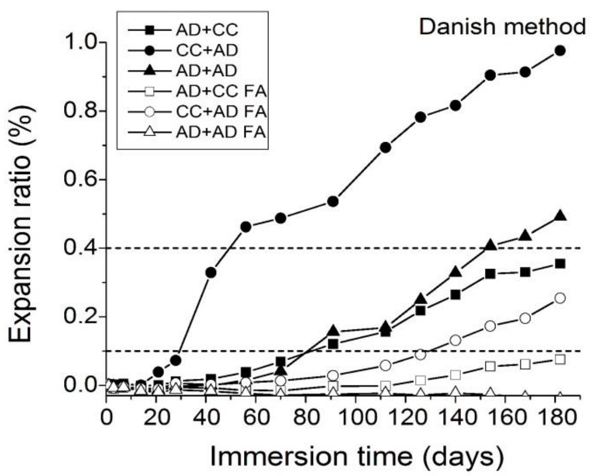


Fig 5. Expansion ratio of concrete prisms tested in Danish test method

In the behavior of concrete expansion due to ASR, fine cracks begin to visible at rate of 0.05% to 0.1%. In general, the progress of cracking of the specimen in accordance with the increasing rate of concrete expansion. For specimens tested in JIS method, the cracks pattern, only observed on the CC+AD specimen's surface, did not change much starting from 8 weeks of measurement. There are only few cracks were observed. However, the cracks width increased over time. As for specimens tested in Danish method, countless fine cracks, form a map-cracking on the surface of the specimens, could be observed at early stage, especially for CC+AD specimen. The cracks width also increasing accompanied by pop-out as the expansion increasing. This is due to andesite aggregate was being used as fine aggregate. In particular, the occurrence of pop-out is significant in Danish method as shown in Fig. 6. Occurrence of pop-out is regardless of the presence or absence of additional FA due to sodium chloride accumulated on the surface that reacts with fine aggregate, from andesite aggregate, that triggers ASR.

3.2 Modulus of Elasticity of Concrete Specimens

As shown by Figs. 7 and 8, the results of the modulus of elasticity showed good correlation with the expansion results. The reduction of dynamic modulus of elasticity ratio became remarkable at the state which expansion ratio was larger than 0.1%. From this result, the dynamic modulus of elasticity can clearly reflect the deterioration process of concrete due to ASR expansion which may consist with the occurrence and growth of cracks.

Furthermore, a temporary recovery and decreasing of dynamic modulus of elasticity were found, especially for specimens with andesite aggregate as the fine aggregate. This phenomenon possibly occurred due to the ASR gel is in liquid state on the first stage (rich (Na^+ + K^+)), then it can easily react with the hydration product (Substitution of Ca^{2+} to the (Na^+ + K^+)) to make the ASR gel fill the microcracks.

3.3 ASR Gel and Polarizing Microscopic Observation

After completing the accelerated concrete test, ASR gel observation was carried out to measure. ASR gel could be seen on the specimens with large expansion. It is confirming the penetration of alkali solution from outside into concrete specimen. As for the specimens with additional high quality fly ashes, the ASR gel only observed in CC+AD FA specimen. This replacement ratio of fly ashes could be confirmed to be effectively suppressed ASR over a long period of time. Besides suppressing the occurrence of ASR, the salt penetration into the concrete specimens is also reduced. The image of ASR gel observation is shown in Fig. 9.

These findings also backed-up by thin section samples observation with polarizing microscope, as shown by Fig. 10. ASR severity level was increasing in line with the increasing of expansion ratio. For JIS test specimens, continuous network of cracks (<25 μm width) from the aggregate to cement paste filled with ASR gel has been observed in CC+AD specimen (ASR level: III). As for Danish test specimens, large cracks, filled with ASR gel, from the aggregate to

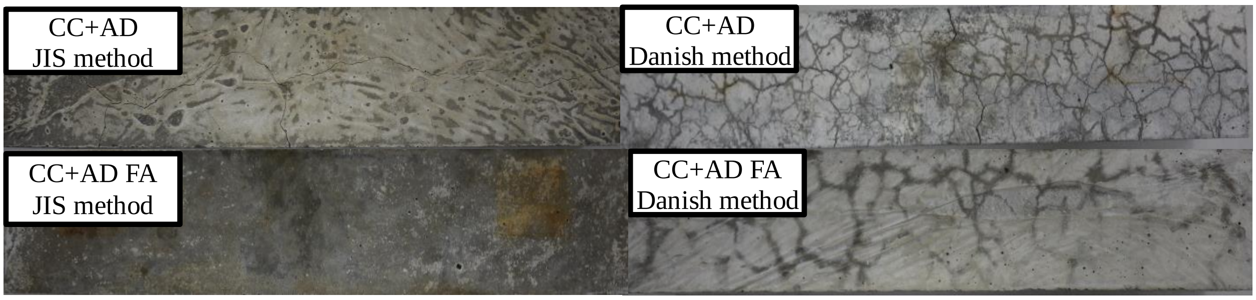


Fig 6. Surface of the specimens after completion of accelerated concrete prims test

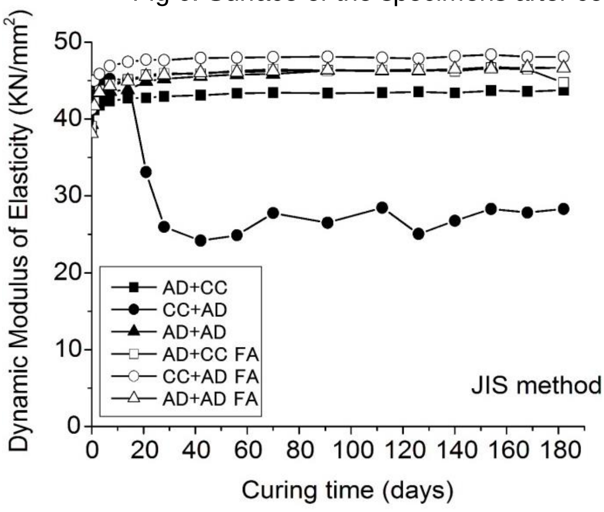


Fig 7. Modulus of elasticity of concrete prisms tested in JIS test method

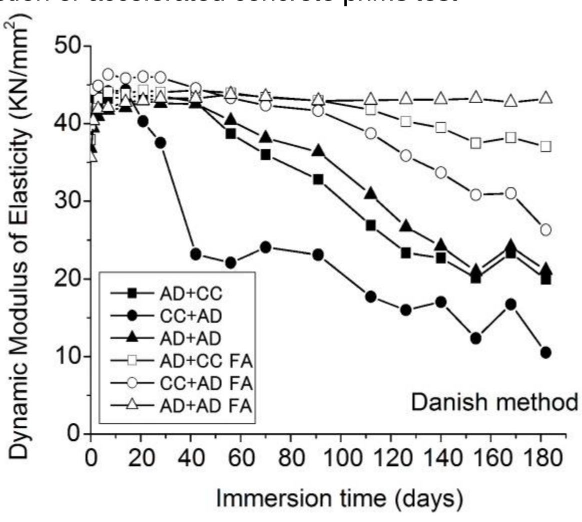


Fig 8. Modulus of elasticity of concrete prisms tested in Danish test method

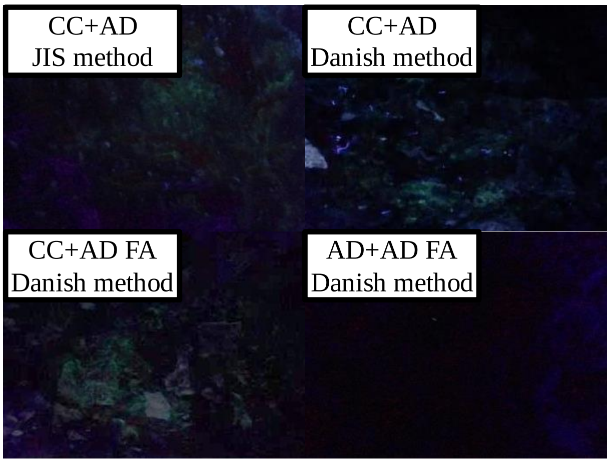


Fig 9. ASR gel formation of concrete prism specimens by uranyl acetate method (observed area: 75 mm x 75 mm)

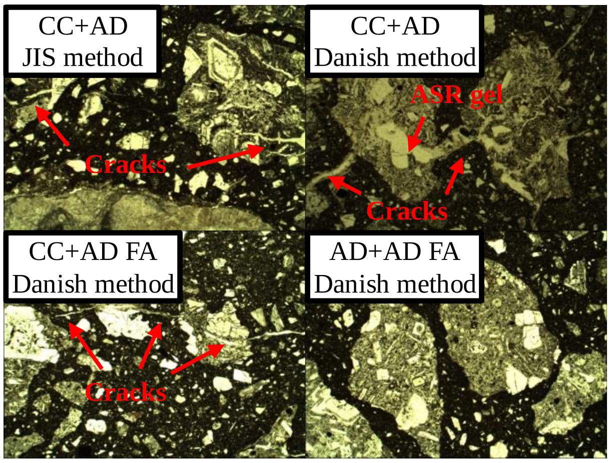


Fig 10. Polarizing microscope observations of concrete prisms thin sections (observed area: 25 mm x 25 mm)

cement paste observed in CC+AD (ASR level: V) and AD+AD (ASR level: IV) specimens. The crack width (<25 μm) and observation of ASR gel decrease in AD+CC and CC+AD FA specimens (ASR level: III). As for AD+CC FA specimen, cracks occurred only inside the aggregate (ASR level: II) and there is no crack and ASR gel could be observed in AD+AD FA specimen. These results add more confidence in the effectiveness of high quality fine fly ashes on ASR mitigation.

4. CONCLUSIONS

Main results obtained in this study are as follows:

(1) The proportion of 40% andesite aggregate and 60% calcium carbonate aggregate shows a pessimum effect which triggers more severe ASR deterioration. It is especially due to the use of andesite aggregate as the fine aggregate.

(2) High quality fly ashes with 15% replacement ratio shows a good ASR mitigation effect, which is a high pozzolanic activity due to very fine particle size and high amount of glass-rich silica phase.

(3) The finesses of this fly ashes increase the alkali adsorption by CSH gel and also make the specimens denser which has a great contribution to the inhibitory effect of ASR.

(4) The dynamic modulus of elasticity, uranyl fluorescence method and thin sections observation are found to improve the measurement accuracy of the deterioration degree of concrete due to ASR.

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